Introduction to Compound Specific Isotope Analysis (CSIA)

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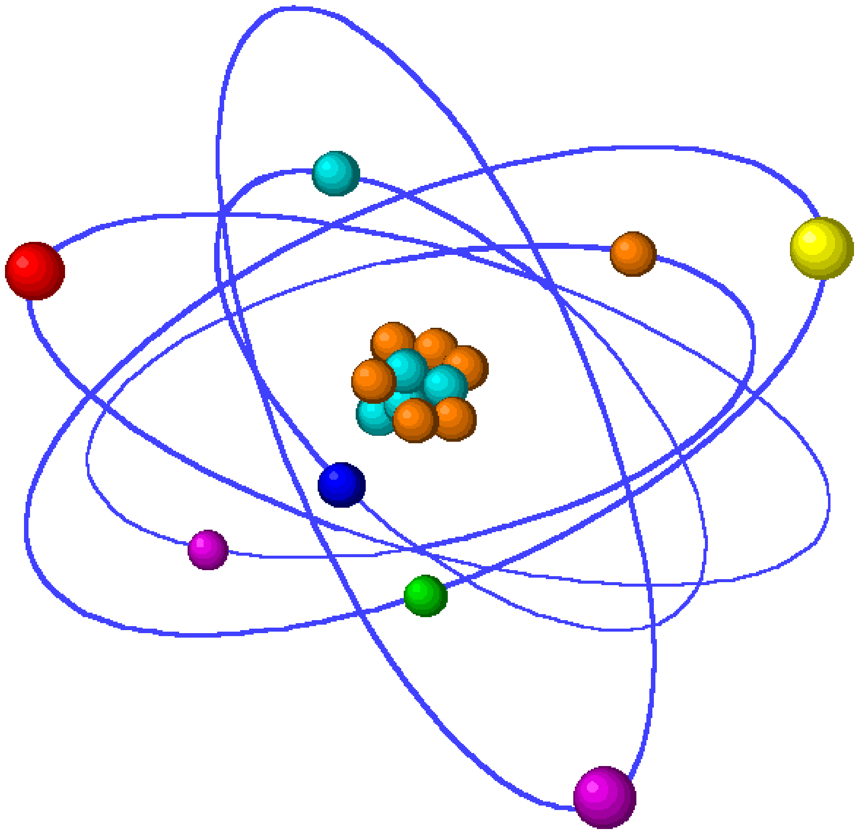
Presentation Outline

1. Stable Isotopes: Basic Concepts and Definitions
2. Determination of the Isotope Ratios
3. Isotope Composition of Env. Contaminants
4. Applications: Source ID
5. Applications: Degradation assessment

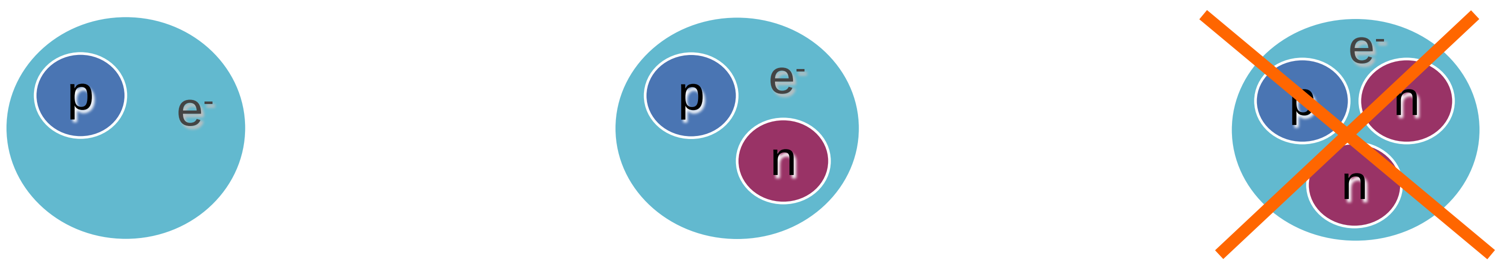
1. Stable Isotopes: Basic Concepts and Definitions



What are Stable Isotopes?

- Isotopes have the same number of protons – identical atomic number
- Isotopes have different number of neutrons – different atomic mass
- Stable isotopes do not undergo radioactive decay – tritium is not a stable isotope

Example: Hydrogen



Hydrogen, ^{1}H

Deuterium, ^{2}H, D

Tritium, ^{3}H, T

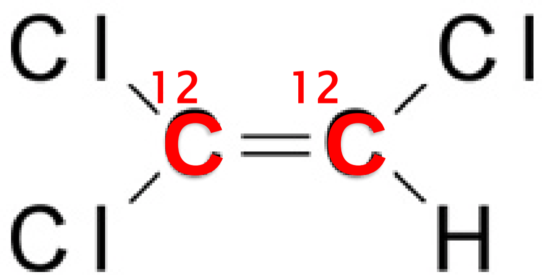
Stable Isotopes of Interest

Isotopic abundances:

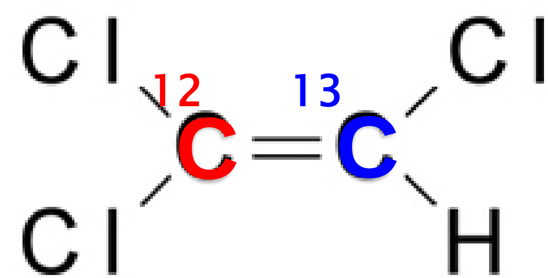
- ^{12}C 99%, ^{13}C 1 %
- ^{1}H 99.985%, ^{2}H 0.014 %
- ^{35}Cl 75.5%, ^{37}Cl 24.5 %

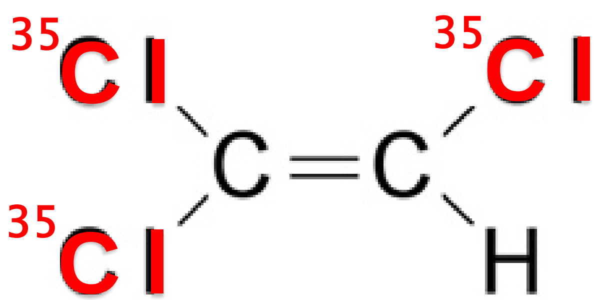
Isotopes within Contaminant Molecules

Trichloroethylene:

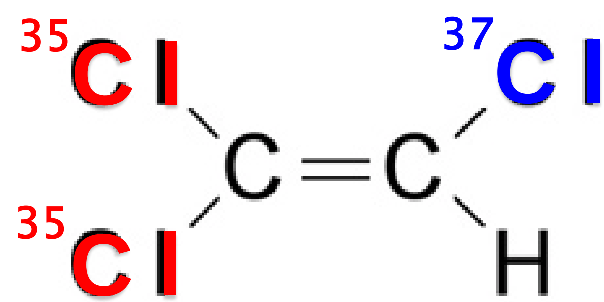


^{12}C vs ^{13}C





^{35}Cl vs ^{37}Cl



Properties of Isotopes

- "Similar" physical and chemical properties.
- Molecules with variable isotope substitutions show identical reaction pathways.

but

- Slightly different rate constants and phase partitioning coefficients.

↓

Reactions often result with <u>isotope fractionation</u>

Isotope Ratios: Delta Notation Example of Carbon Isotope Ratio

$$\delta^{13}C = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000 \quad (‰)$$

$R = {}^{13}C/{}^{12}C$ ($R_{standard}$ is 0.0112372)

$\delta^{13}C$ of –30‰ means that ${}^{13}C/{}^{12}C$ of sample is 30‰ lower than ${}^{13}C/{}^{12}C$ of the standard.

Stable Isotope Ratios: Understanding the Jargon

VSMOW Standard

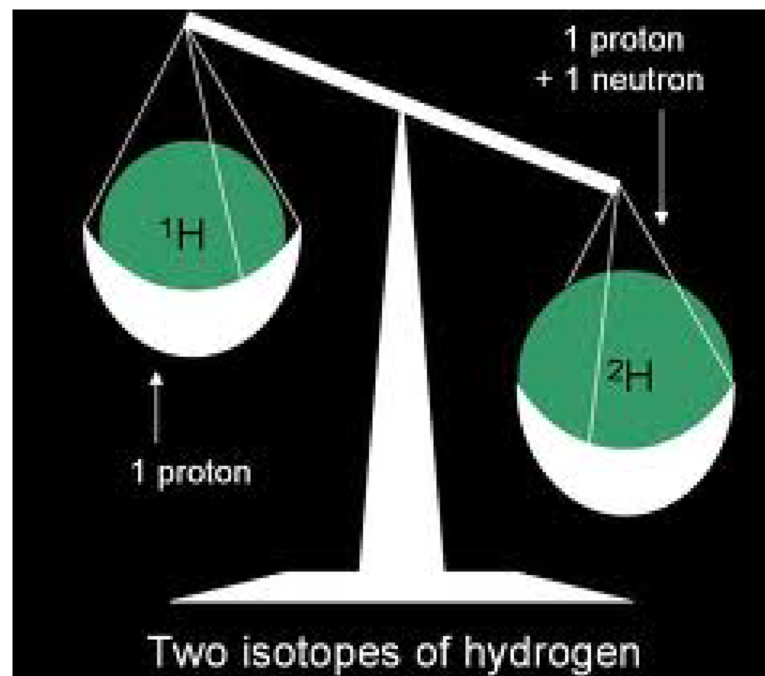
-50.00 -40.00 -30.00 -20.00 -10.00 0.00 10.00

δ^2H

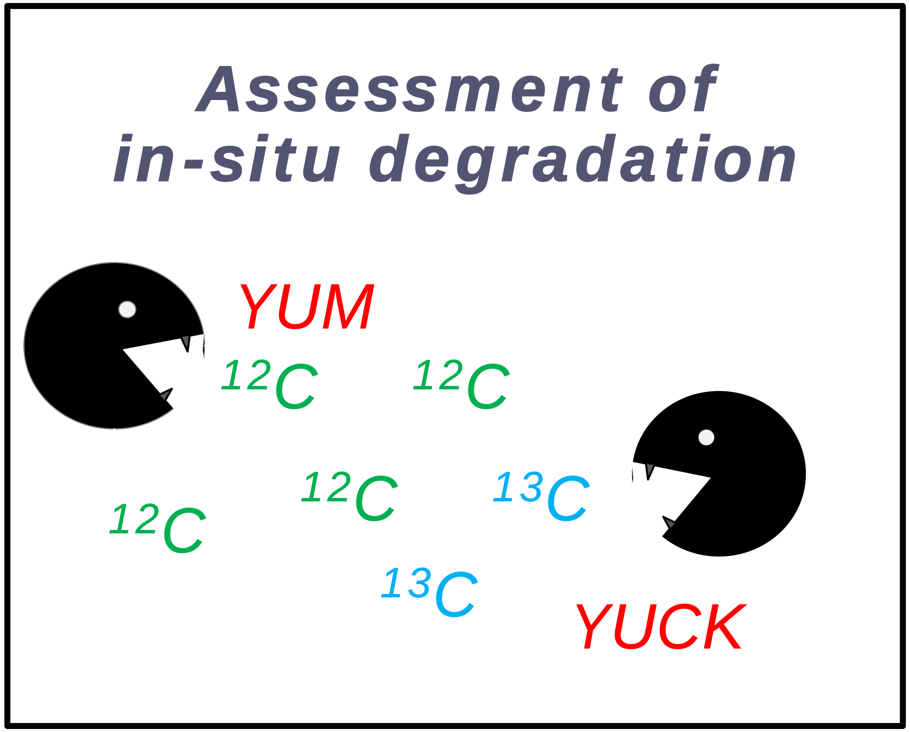
Isotopically lighter

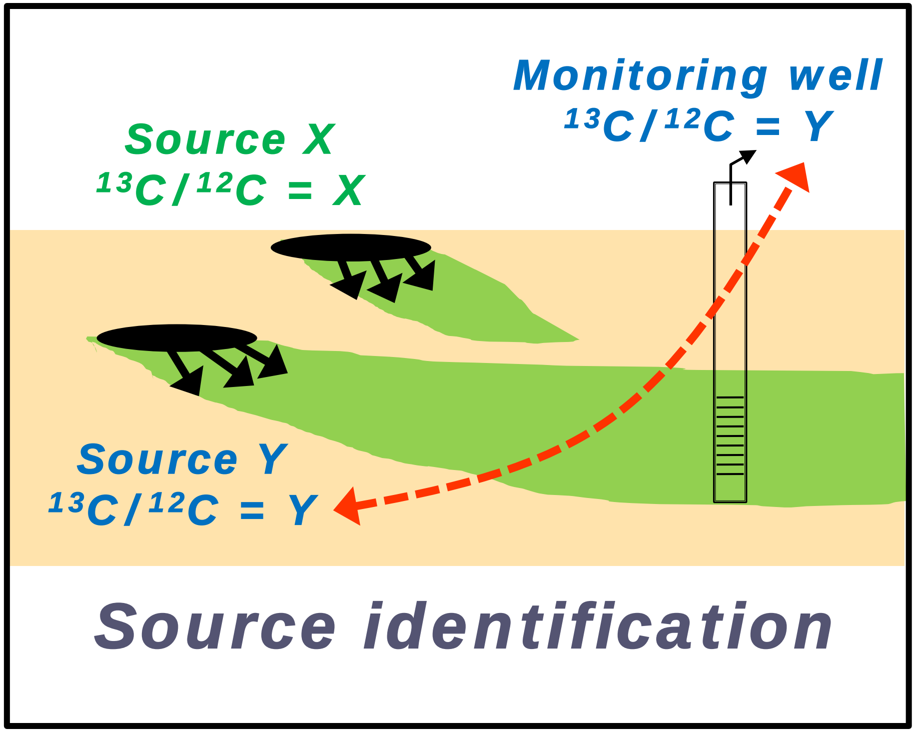
Isotopically depleted

More negative



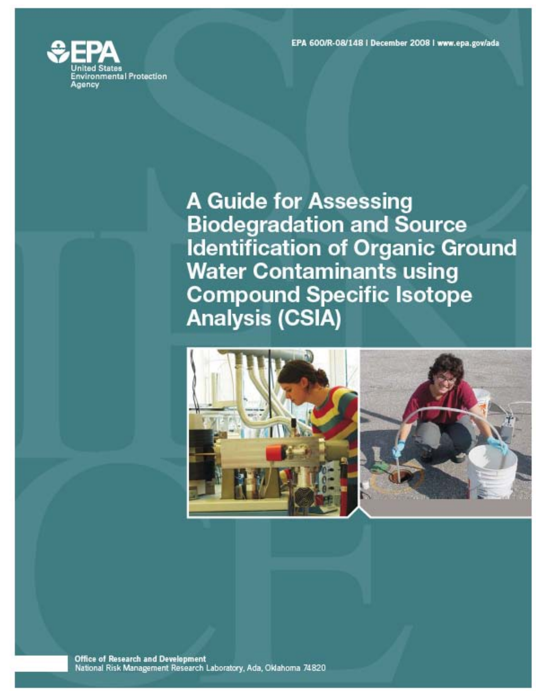
CSIA Applications in Contaminant Studies



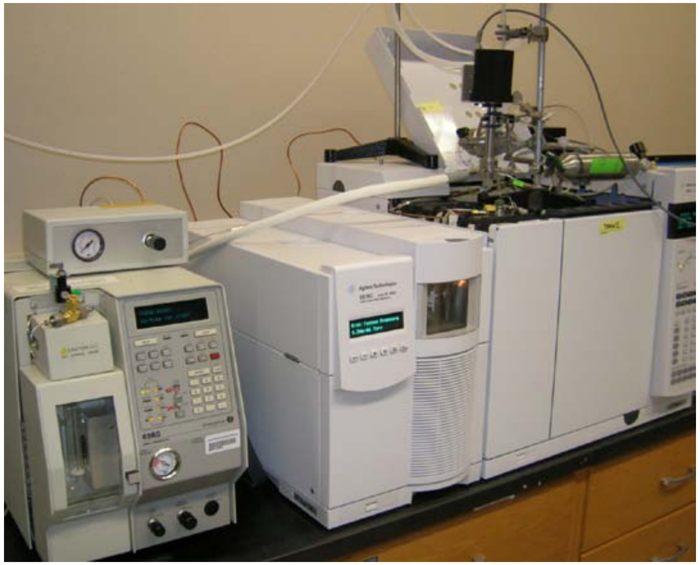


CSIA Guidance Document USEPA, 2008

"Currently, CSIA is in transition from a research tool to an applied method that is well integrated into comprehensive plans for management of contaminated sites"

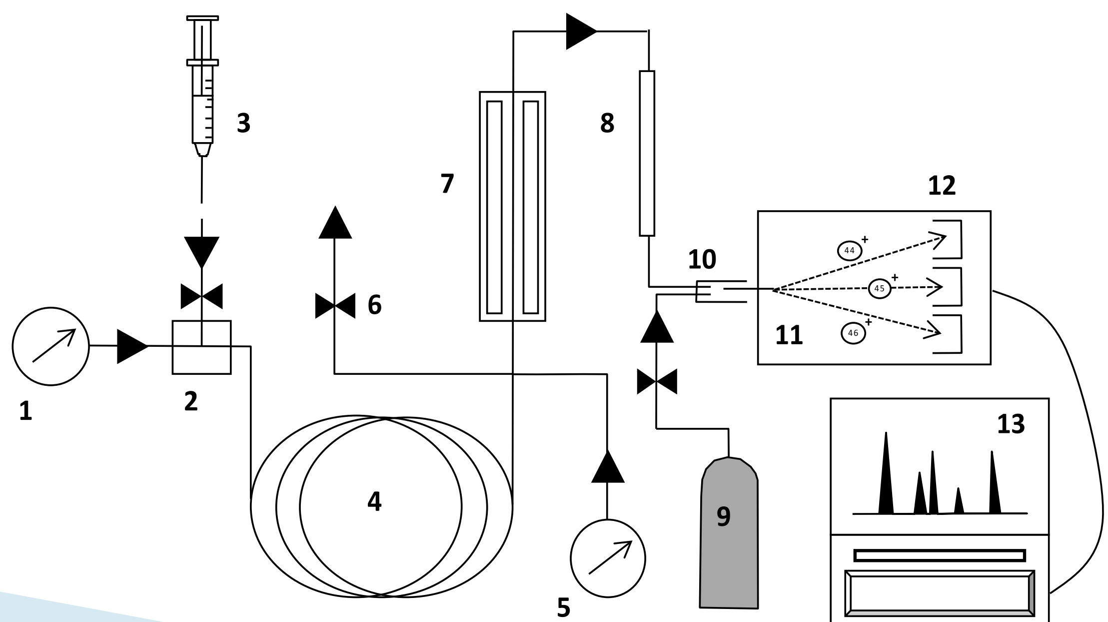


2. Determination of isotope ratios



Compound-Specific Isotope Analysis (CSIA)

- Permits determination of isotope ratios in individual compounds present in sample matrix
- Combination of chromatography with isotope ratio mass spectrometry.
- To work with environmental samples, CSIA has to be optimized for sensitivity and matrix resolution.



Considerations for Environmental Chlorinated Hydrocarbons

- Methods of VOCs extraction are adopted from conventional VOCs methods. Best performance to date: purge and trap (adopted from EPA 524) for aqueous VOCs, adsorbent preconcentration/thermal desorption (adopted from TO-17) for air VOCs.

- For carbon and chlorine CSIA, well-optimized CSIA methods permit detection limits comparable to those of USEPA 8260.

- For hydrogen CSIA, CSIA requires relatively large mass of analyte in comparison with concentration analysis. Detection limits worse by about 1-2 orders of magnitude.

- Generally, analytes amenable to 524 or TO-17 can be expected to be amenable to CSIA. Several commercial options are available for analysis of aqueous chlorinated ethenes. Inquire about less common analytes or air VOCs.

CSIA of Chlorinated Ethenes: Detection Limits for High-Precision CSIA

(based on recent OU methodology for aqueous samples)

<u>Carbon and Chlorine CSIA</u>

VC 1 ug/L

DCE, TCE, PCE 1 ug/L*

<u>Hydrogen CSIA</u>

VC, DCE 10 ug/L

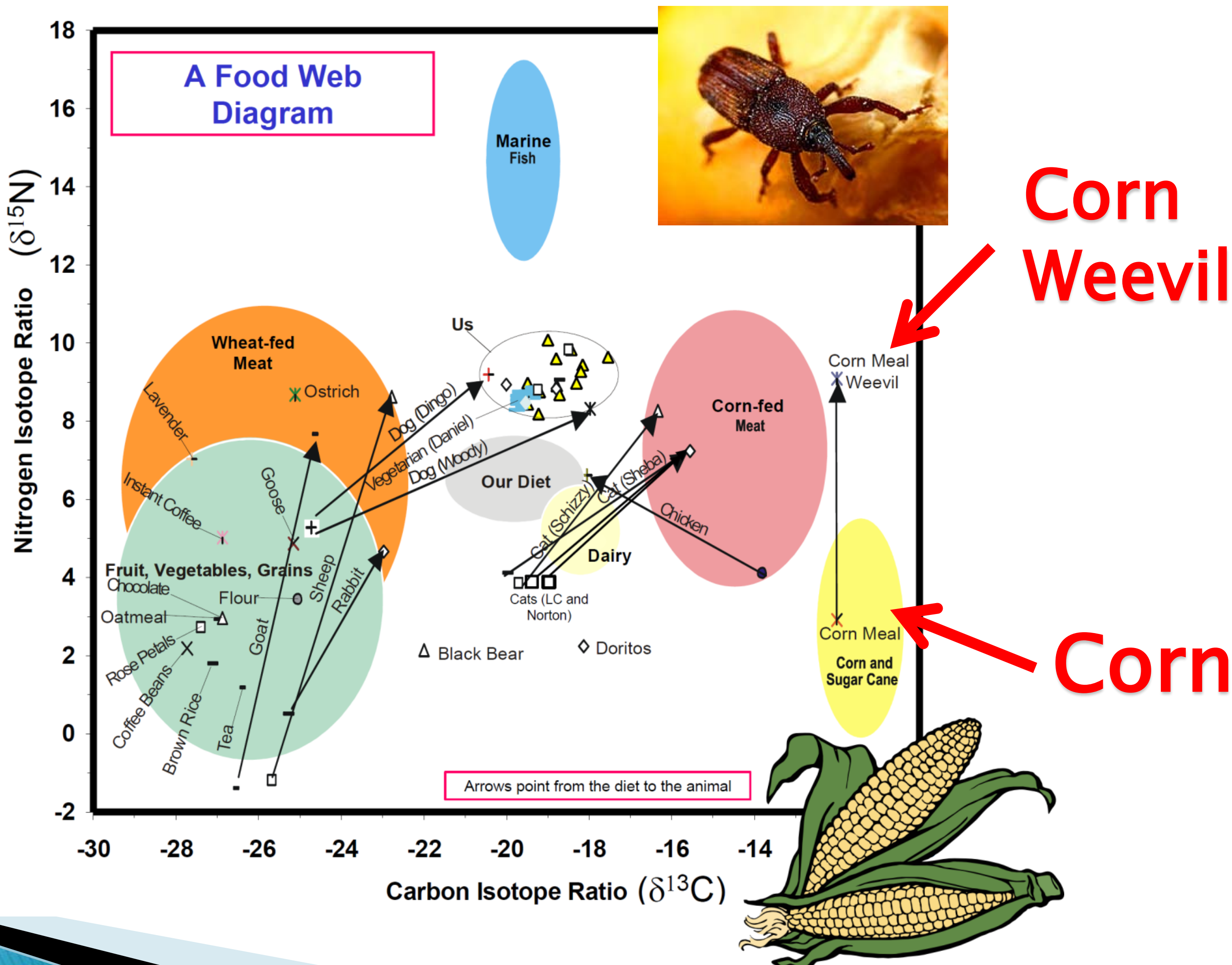
TCE 30 ug/L

* 0.5 ug/L if larger volume of sample is available

3. Stable Isotope Ratios of Synthetic Chemicals

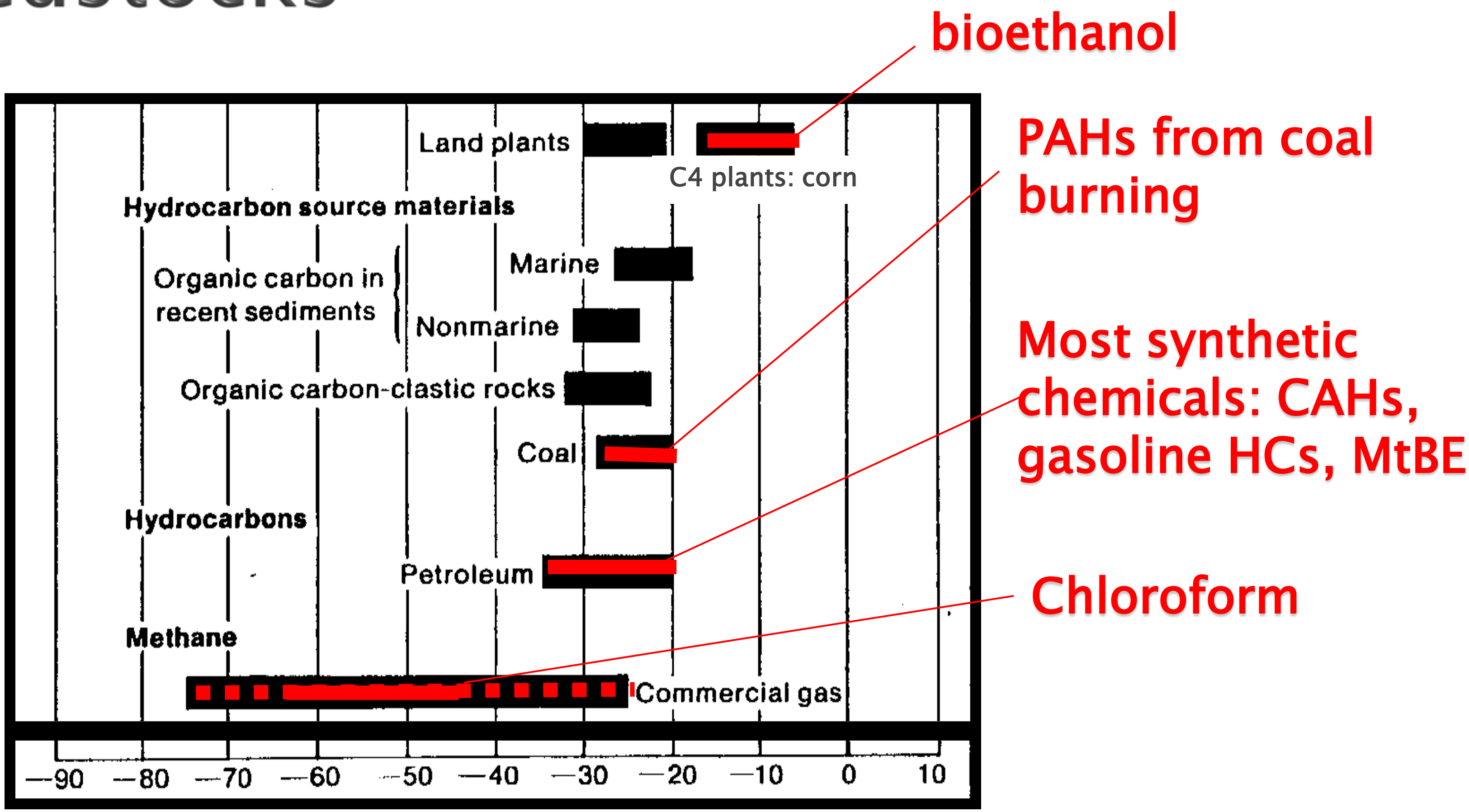
Isotopes – you are what you eat*

* works best for C isotopes



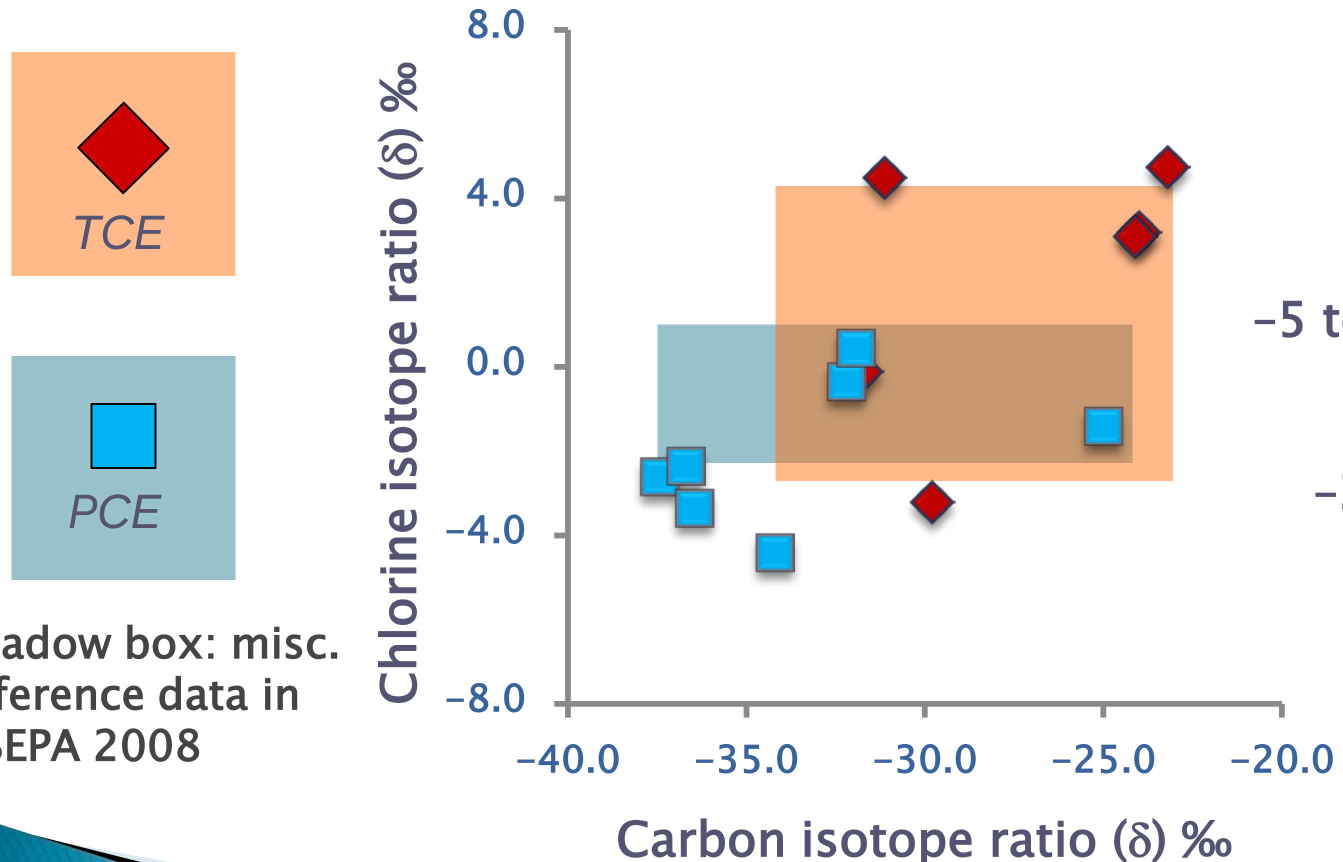
after USGS.gov

The Isotopes in Manufactured Chemicals are Inherited from Synthetic Feedstocks



Carbon isotope Ratios

C and Cl Isotope Ratios in Manufactured Chlorinated Ethenes (recent OU and misc. references)

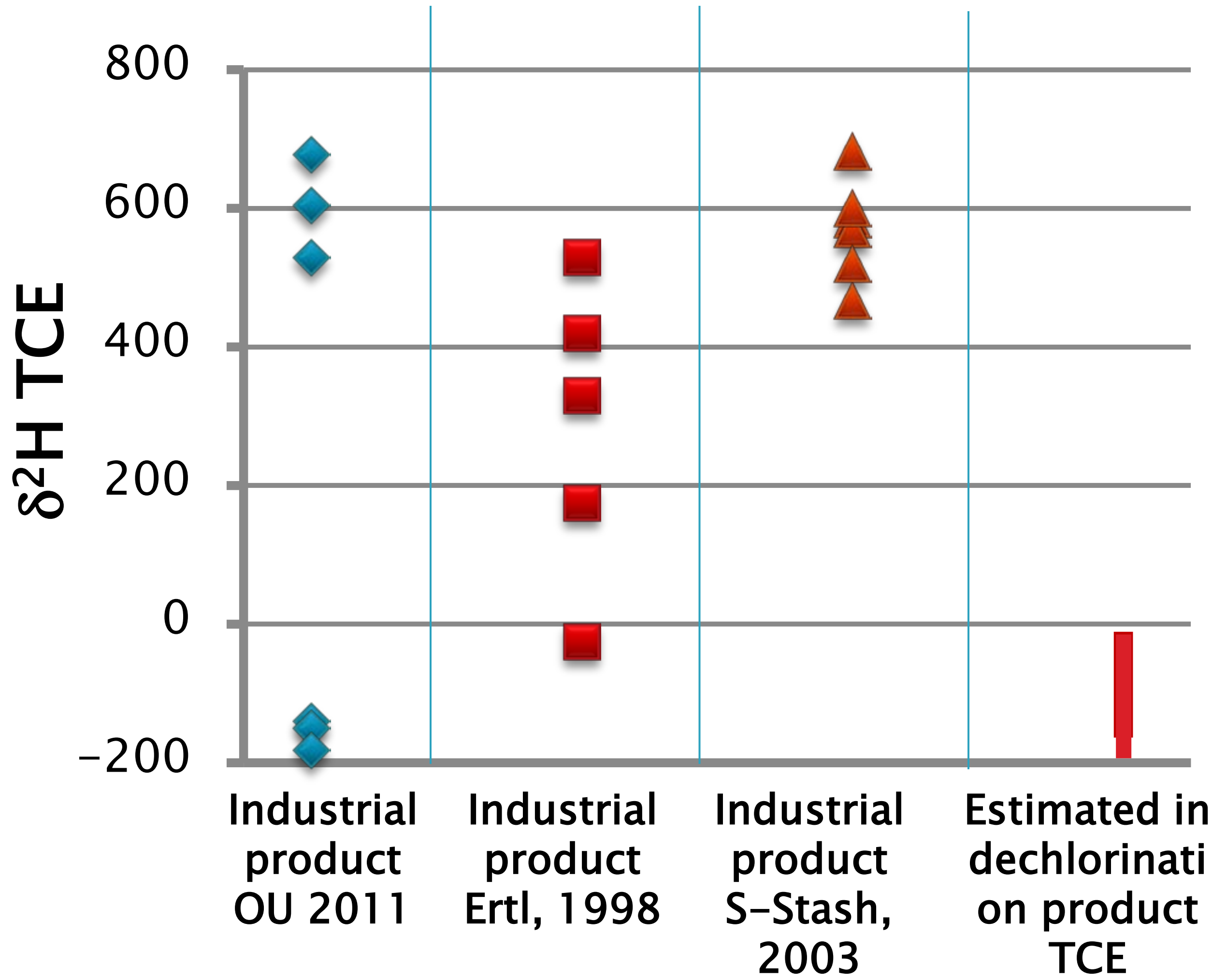


Shadow box: misc. reference data in USEPA 2008

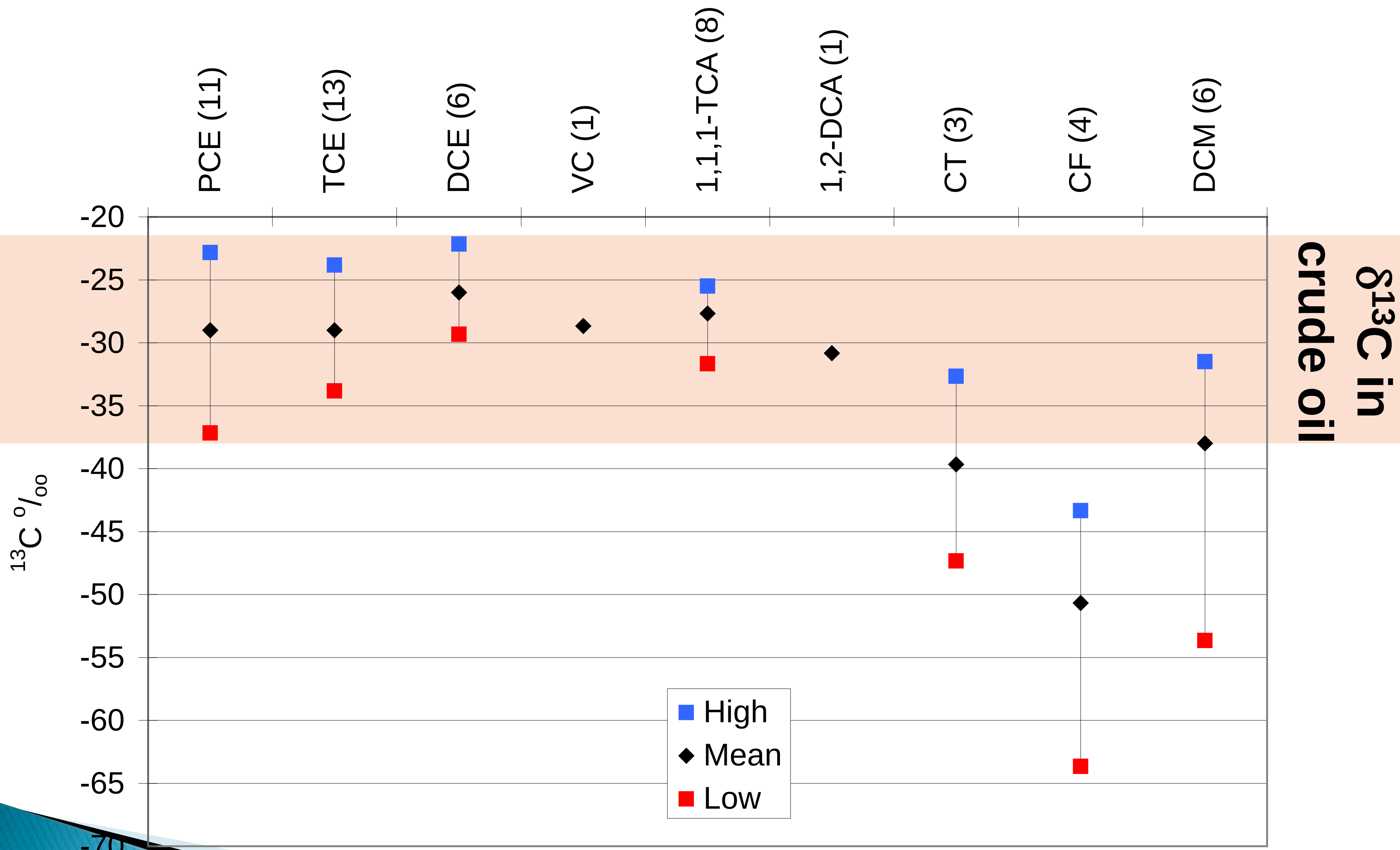
Chlorine
−5 to +5 d37Cl ‰ SMOC

Carbon
−38 to −23 d13C ‰ VPDB

H Isotope Ratios of Manufactured TCE



C Isotope Ratios of Misc. CAHs

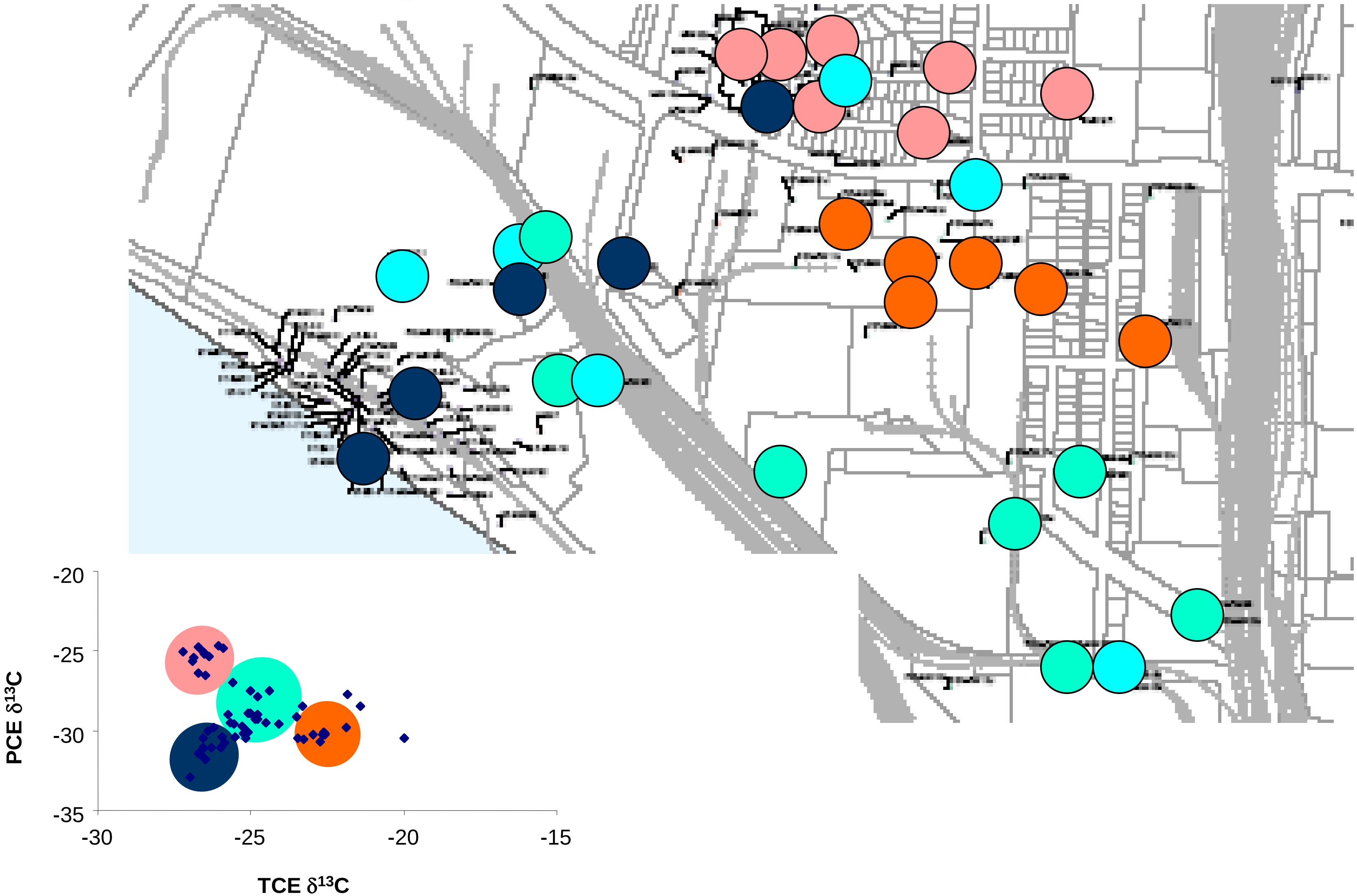


after USEPA 2008

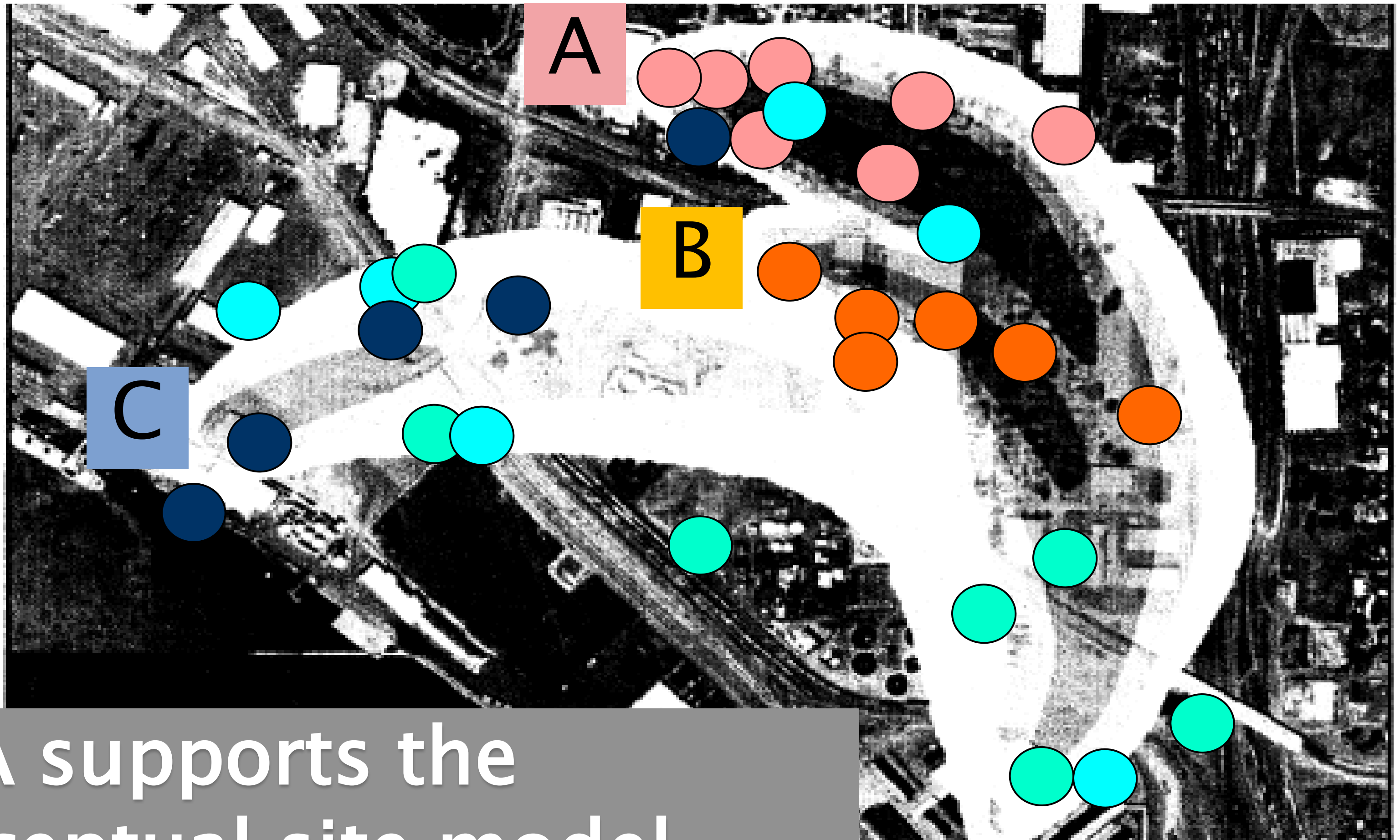
3. Applications of CSIA in Contaminant Source Tracking

?

Isotope fingerprinting of TCE and PCE plumes



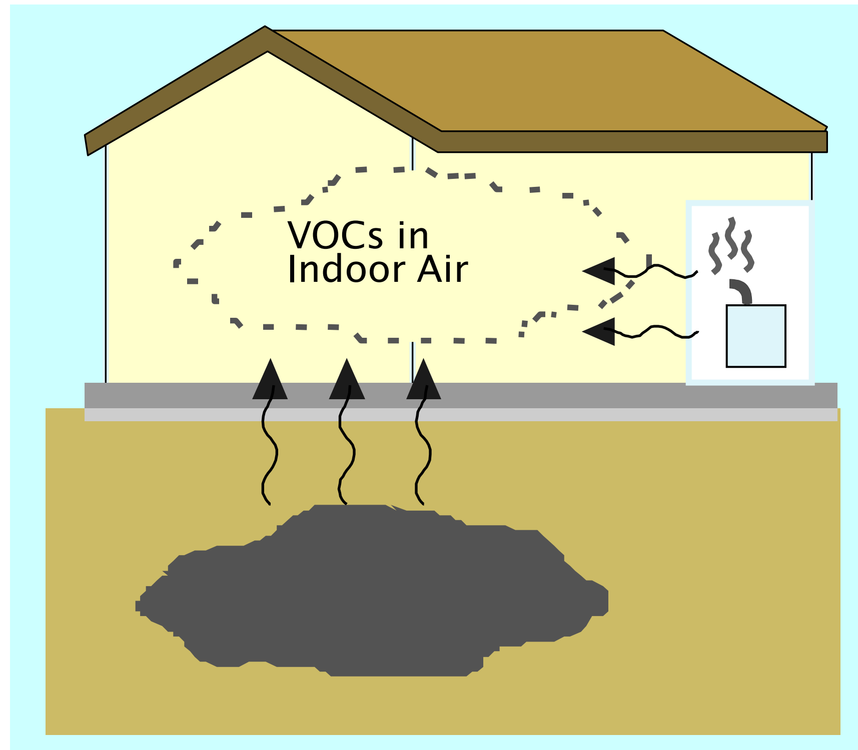
Isotope fingerprinting of TCE and PCE plumes



CSIA supports the conceptual site model

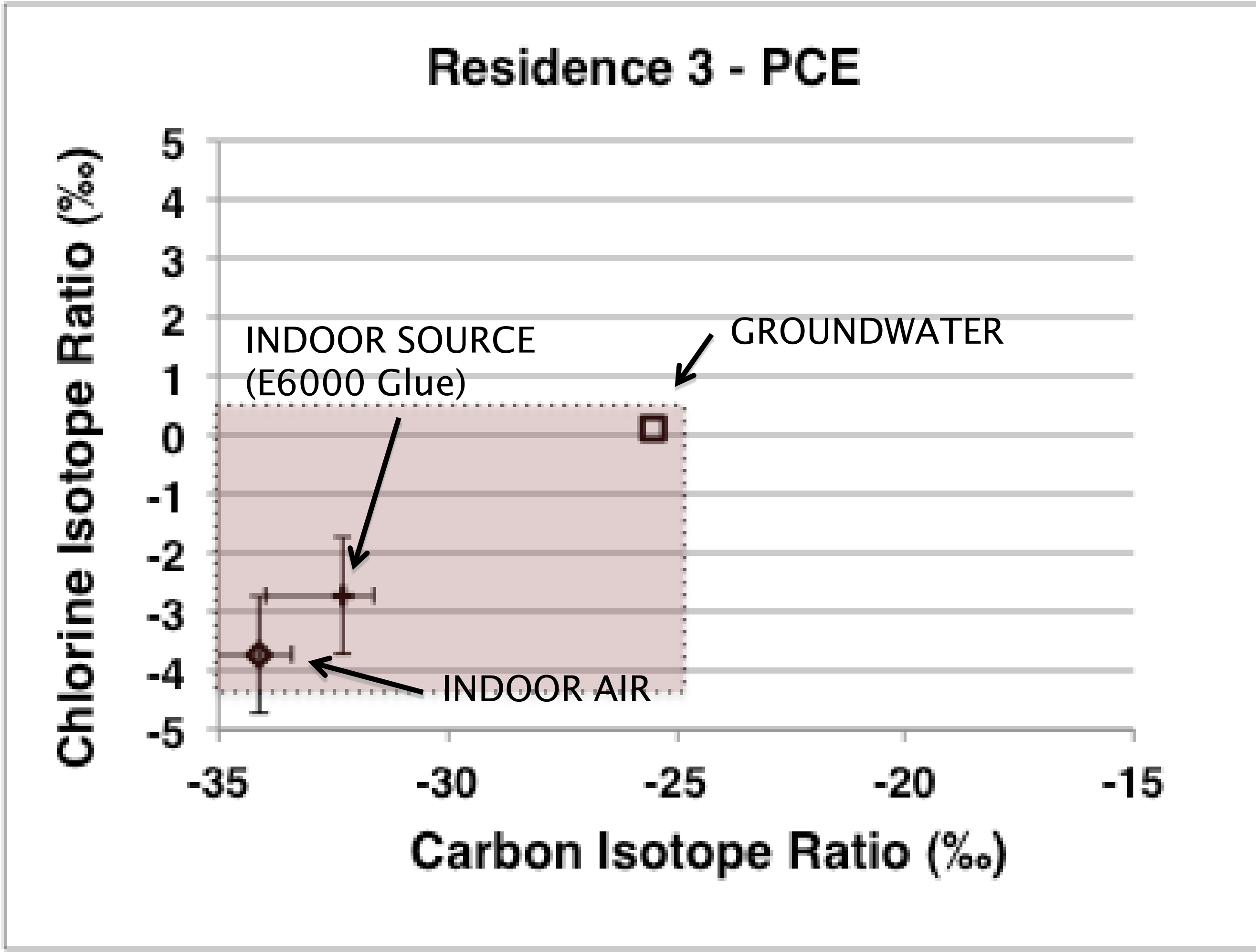
Vapor Intrusions

- At vapor intrusion site, testing of indoor air is most direct way to identify VI impacts.
- Indoor sources of VOCs are ubiquitous: cleaners, glues, plastic, etc
- Detection of VOCs in indoor air does not necessarily indicate vapor intrusion.



Key Point: *Critical need for reliable methods to distinguish between vapor intrusion and indoor sources of VOCs.*

VI Field Demonstration: Hill AFB



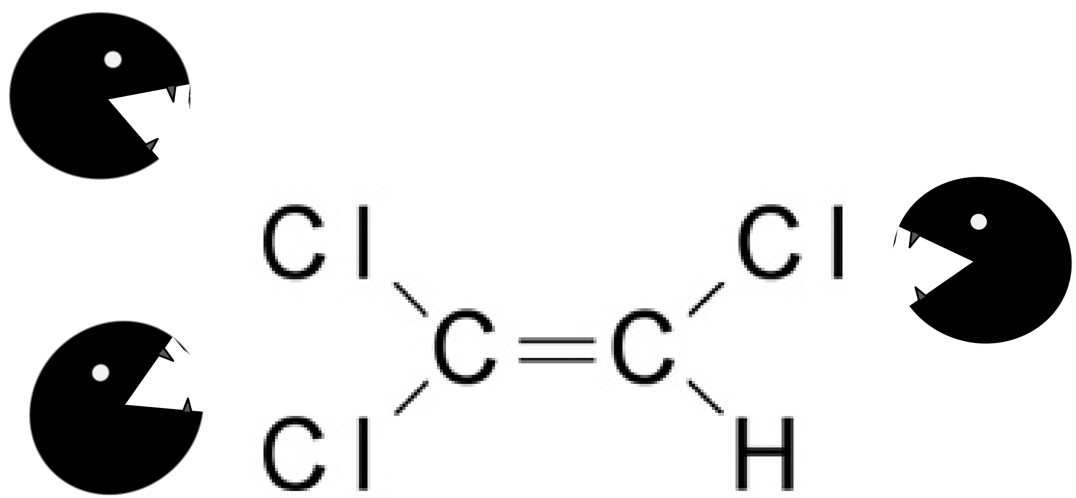
FINDING:

PCE in indoor air is from indoor source.

(Source later identified as E6000 glue)

after McHugh et al., ES&T 2011

5. Applications of CSIA in Contaminant Remediation Assessment



Isotope Fractionation

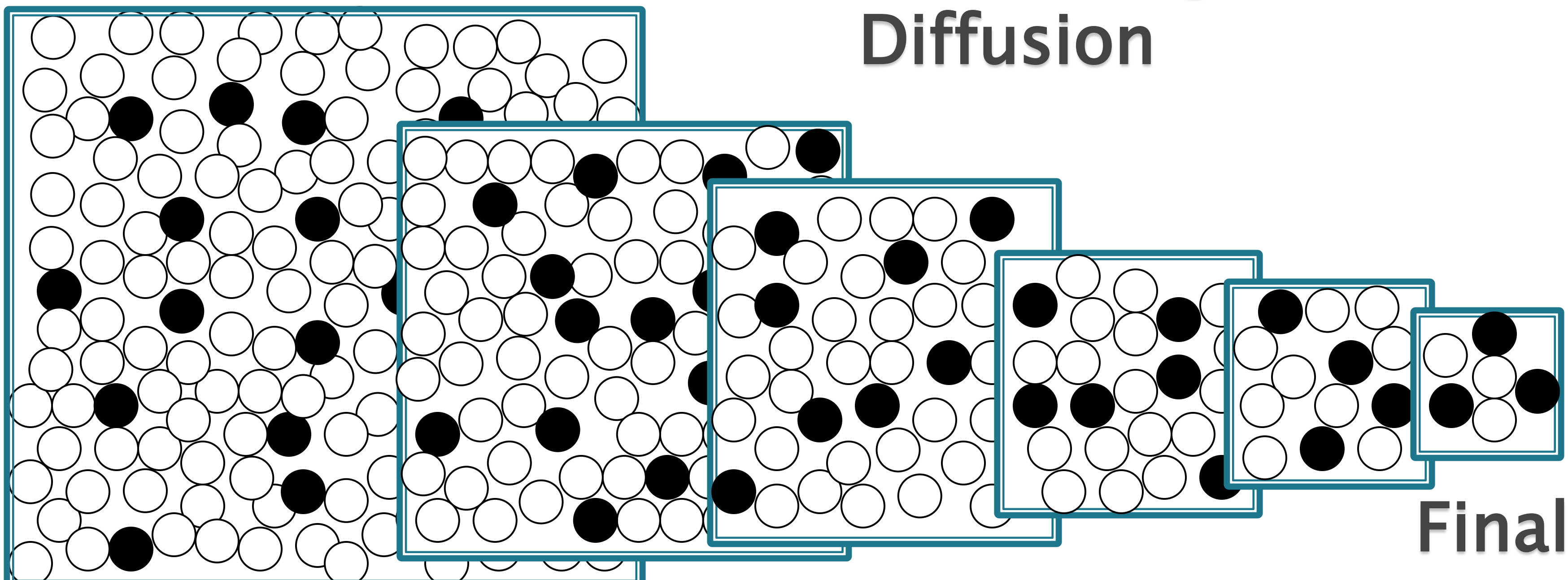
Isotope fractionation is an enrichment of one isotope relative to another in a chemical or physical process. There are two categories of isotope effects: kinetic and equilibrium.

Kinetic Isotope Fractionation

Rate of removal of ○ faster than that of ●

$k_{\bullet} / k_{\circ} = \text{const.}$

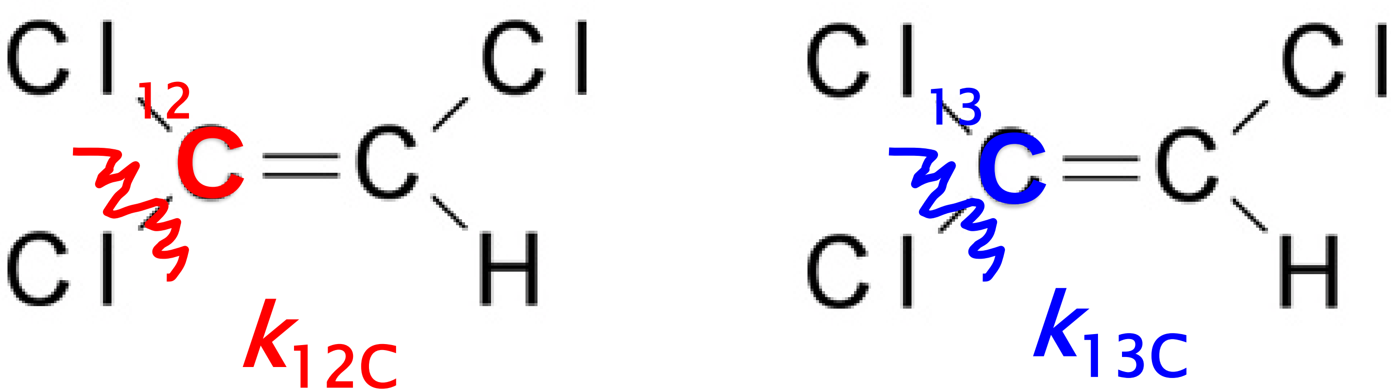
Biodegradation
Chem. Degradation
Diffusion



Final

Initial

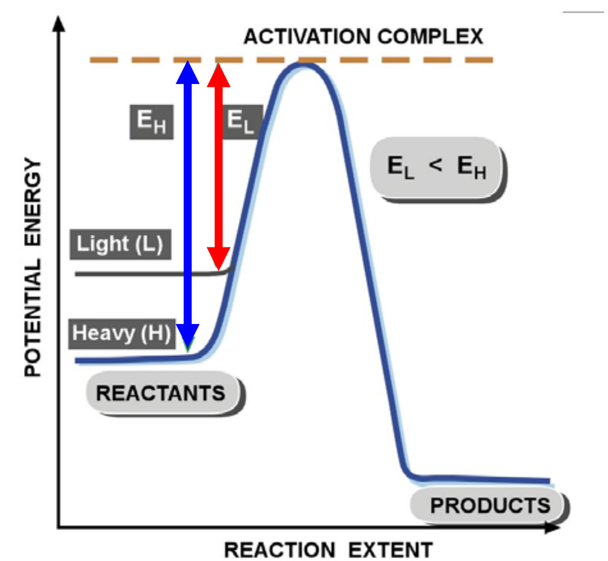
Kinetic Isotope Effect in Contaminant (Bio)Degradation



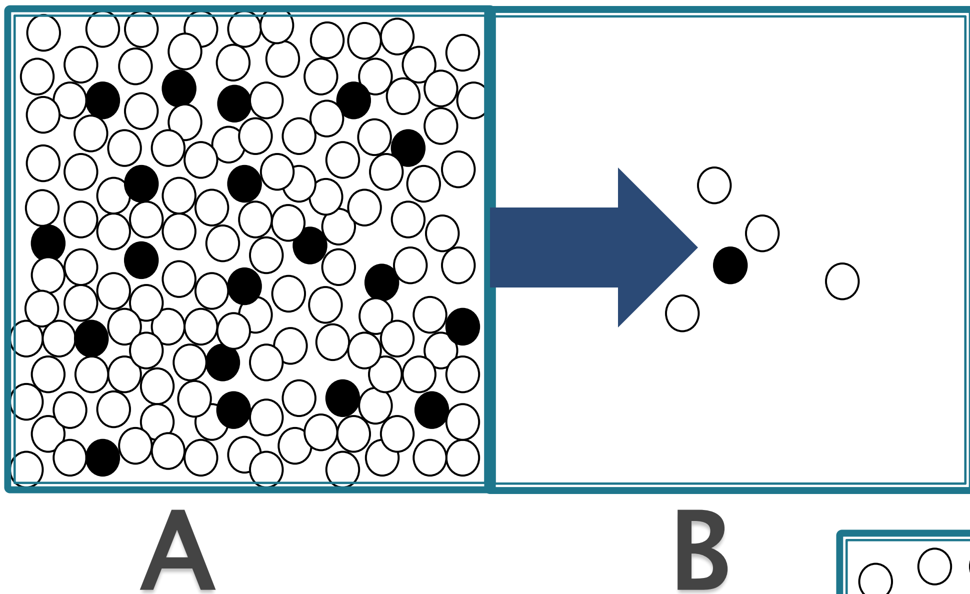
Activation energy for the bond with the lighter isotope is lower.

$k_{12C} > k_{13C}$

Degraded TCE enriched in ^{13}C.



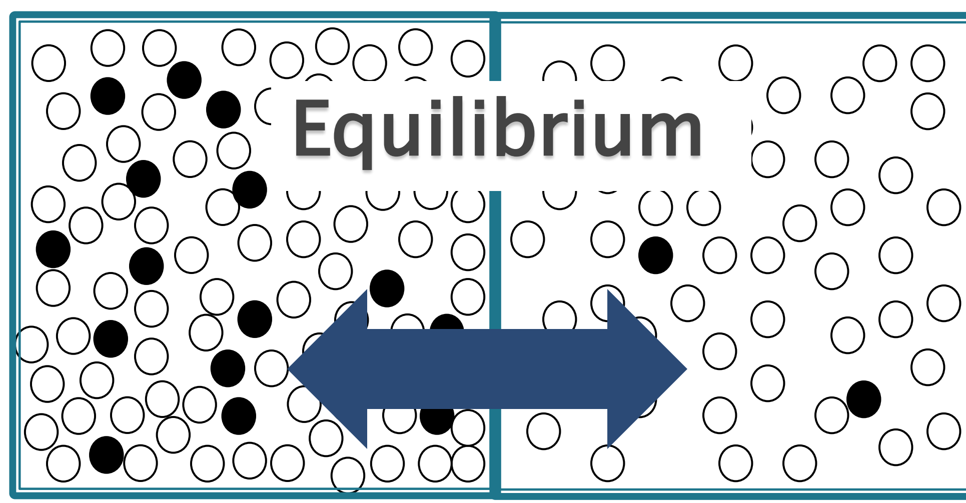
Equilibrium Isotope Fractionation



$K_{\bullet} \neq K_{\circ}$

Phase partitioning
Reversible bio/chem. reactions.

Preferential retention of ● in compartment A



Equilibrium Isotope Fractionation

Differences in **intermolecular forces** between isotopomers control isotope fractionation in phase partitioning.

Light isotopes are more "sticky" and remain in the condensed phase.

May be significant locally, in remediation scenarios involving extensive mass removal through vapor phase.

Rayleigh Model of Kinetic Fractionation

(Lord Rayleigh, 1896)

Mathematical description of isotope fractionation

Provides functional approximation for subsurface degradation

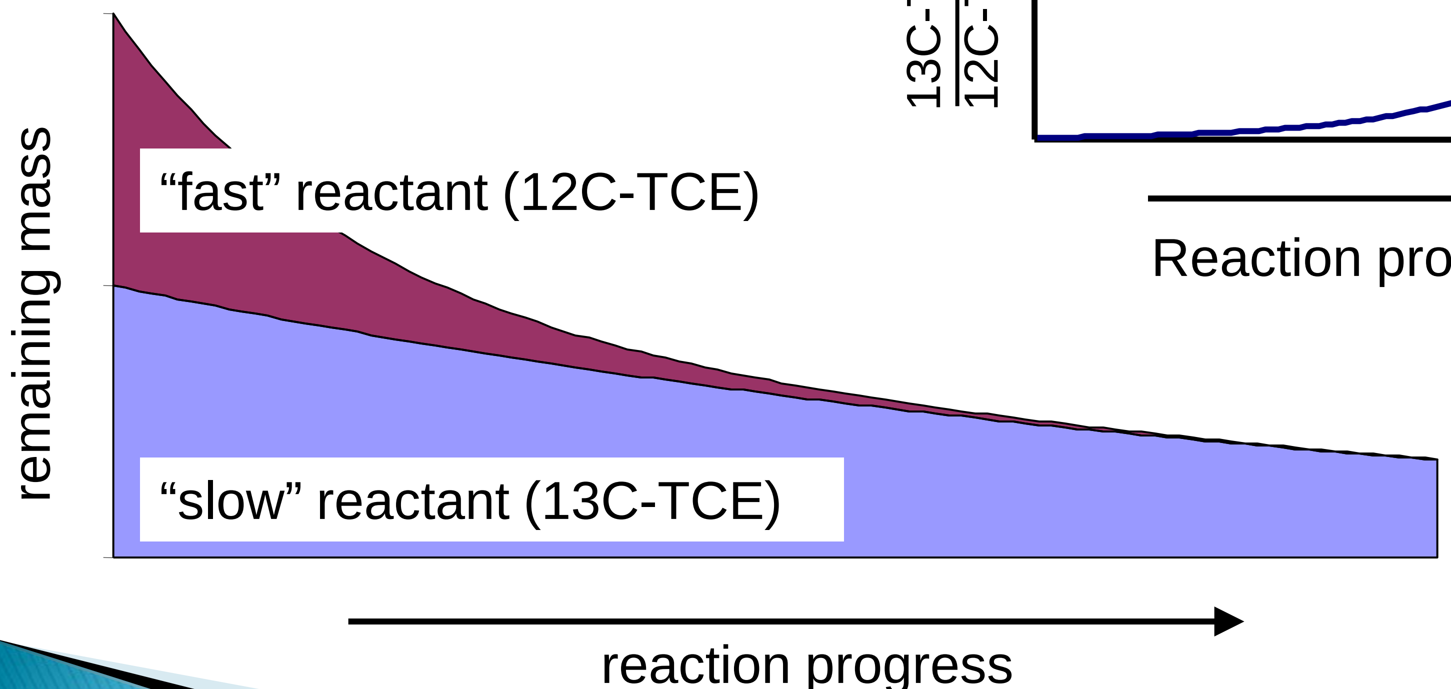
Permits calculation of reactant mass destruction

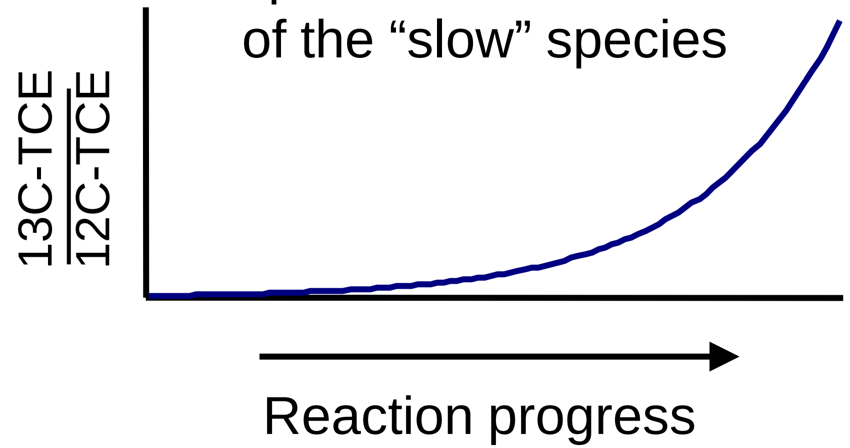
Rayleigh Model of Kinetic Fractionation

(after Rayleigh, 1896)

fractionation factor constant

$$\alpha = {}^{heavy}k / {}^{light}k$$

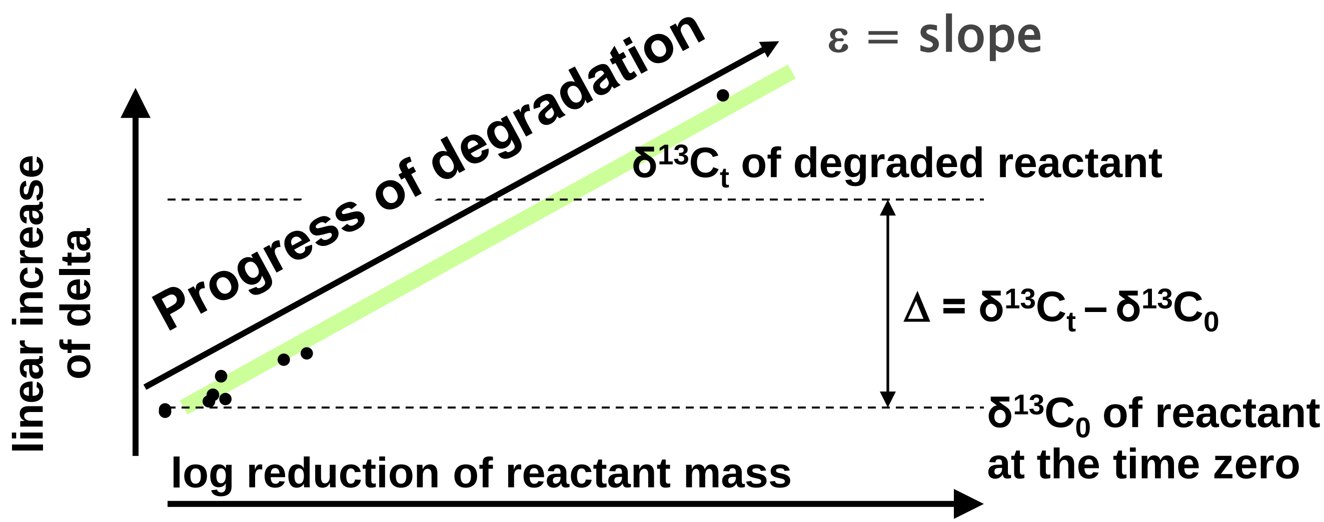




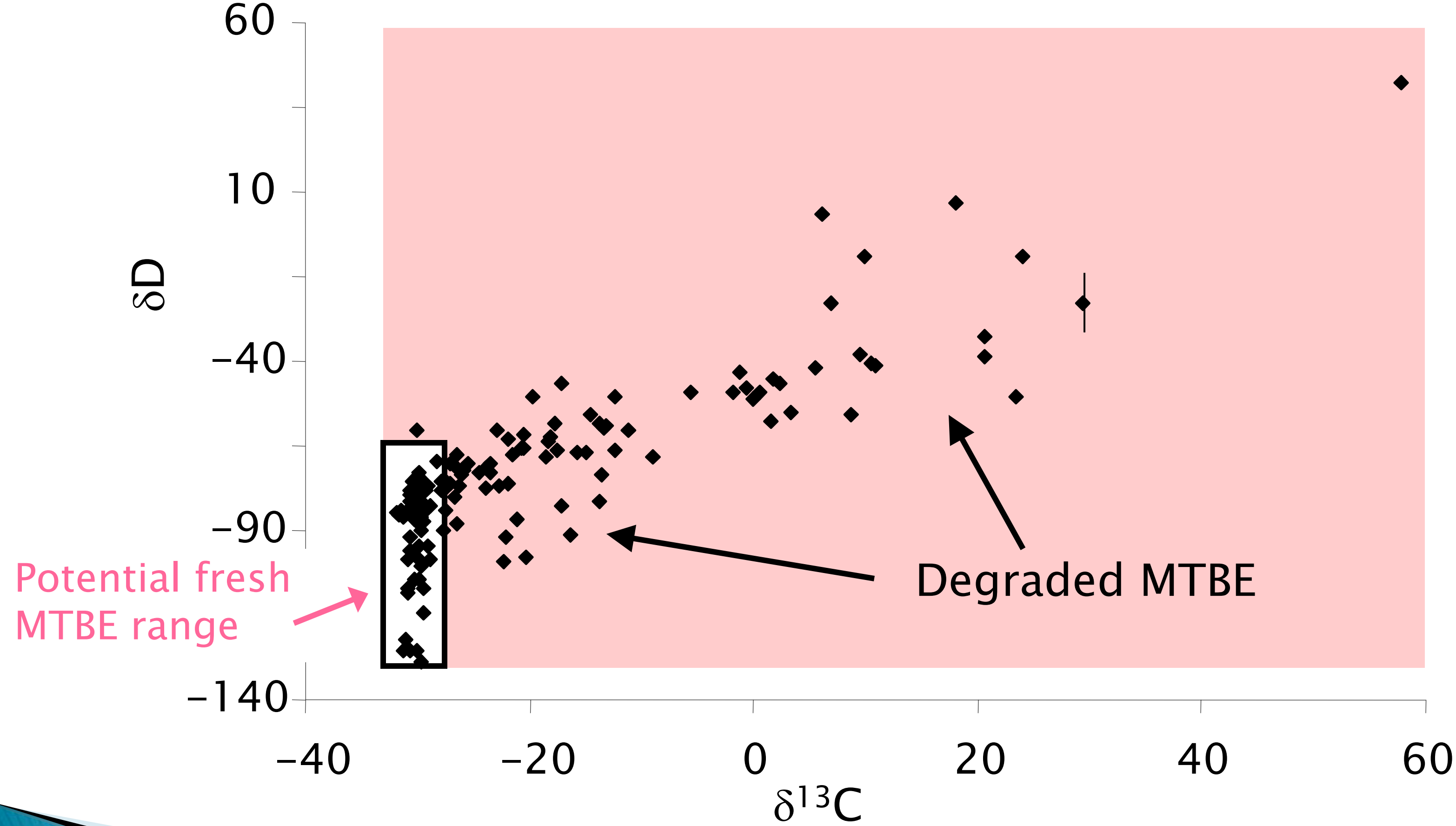
Rayleigh Model of Kinetic Fractionation: Common Notation

$$\delta^{13}C_t = \varepsilon * \ln(\mathrm{Conc.}/\mathrm{Conc.}_0) + \delta^{13}C_0$$

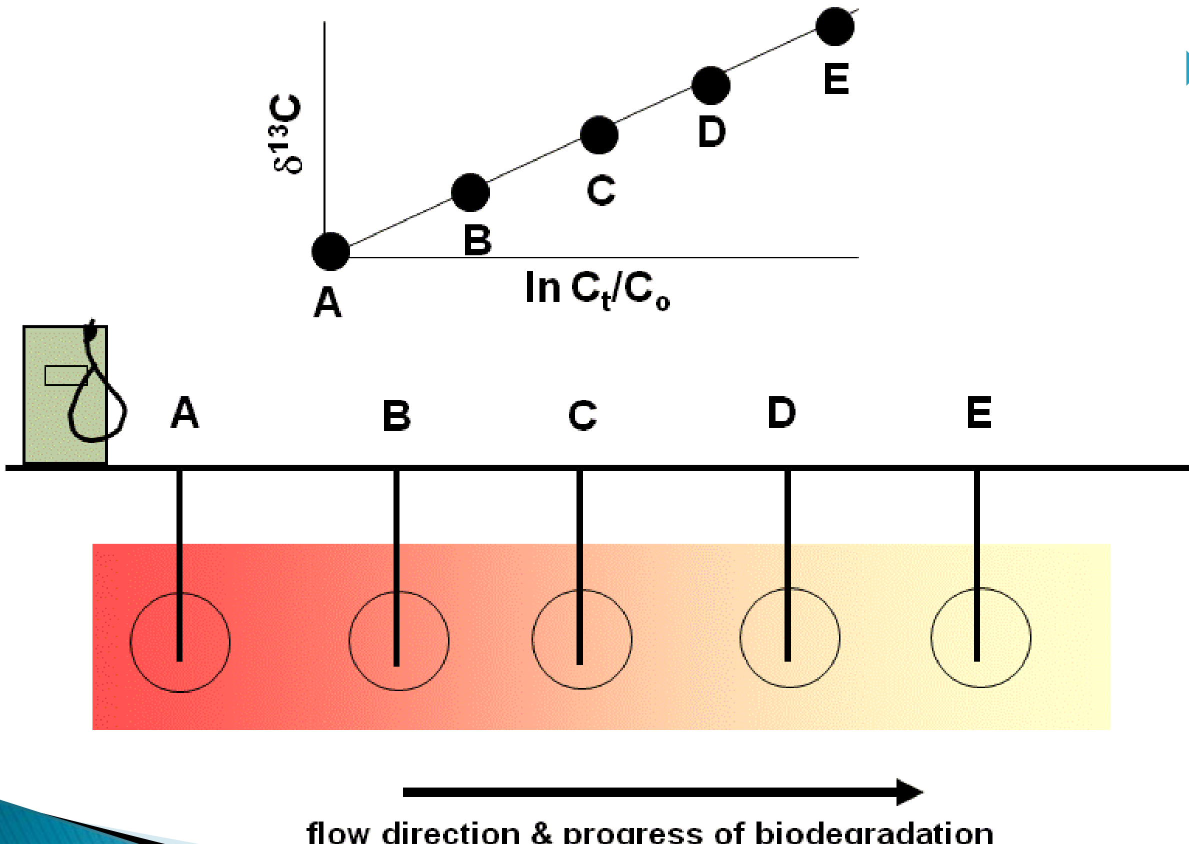
$$\text{enrichment factor } \varepsilon = (\alpha - 1) \times 10^3$$



Using CSIA Data to Detect Degradation: Example of MtBE

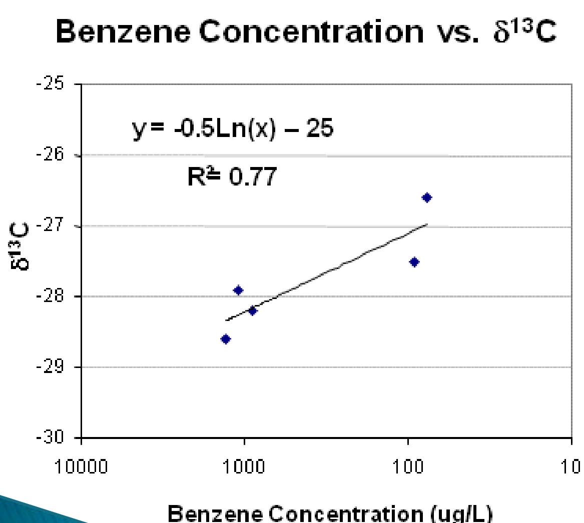


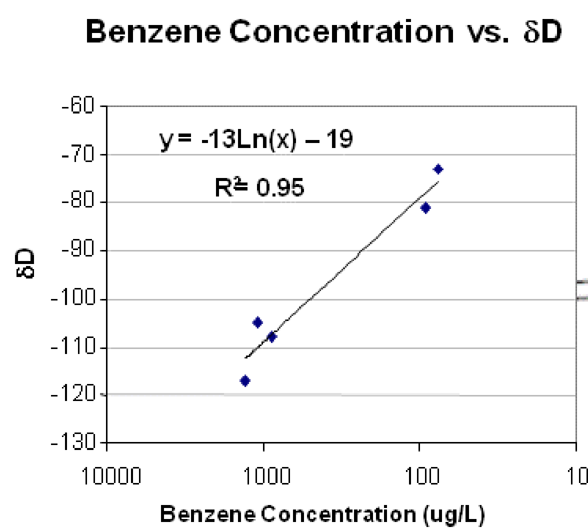
Rayleigh-style Fractionation in a Theoretical Plume

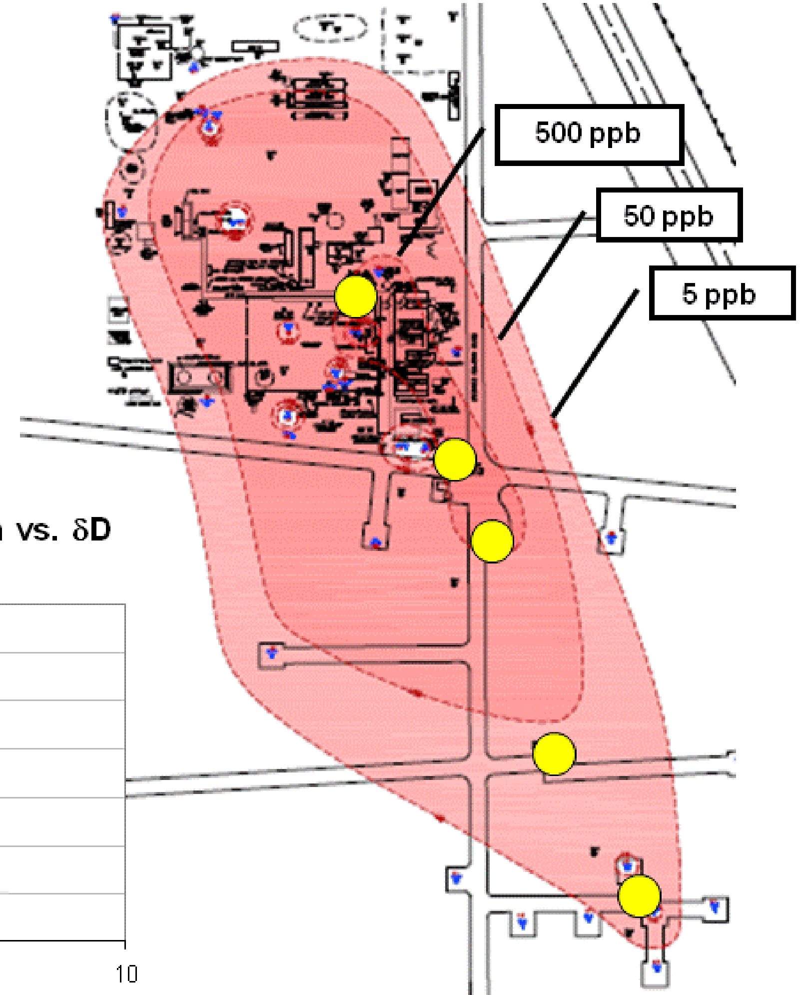


- Close match to Rayleigh Model can be observed if degradation is the predominant mechanism of attenuation

Pretty Good Example from Homogenous Hydrogeology: A Benzene Plume in Thailand

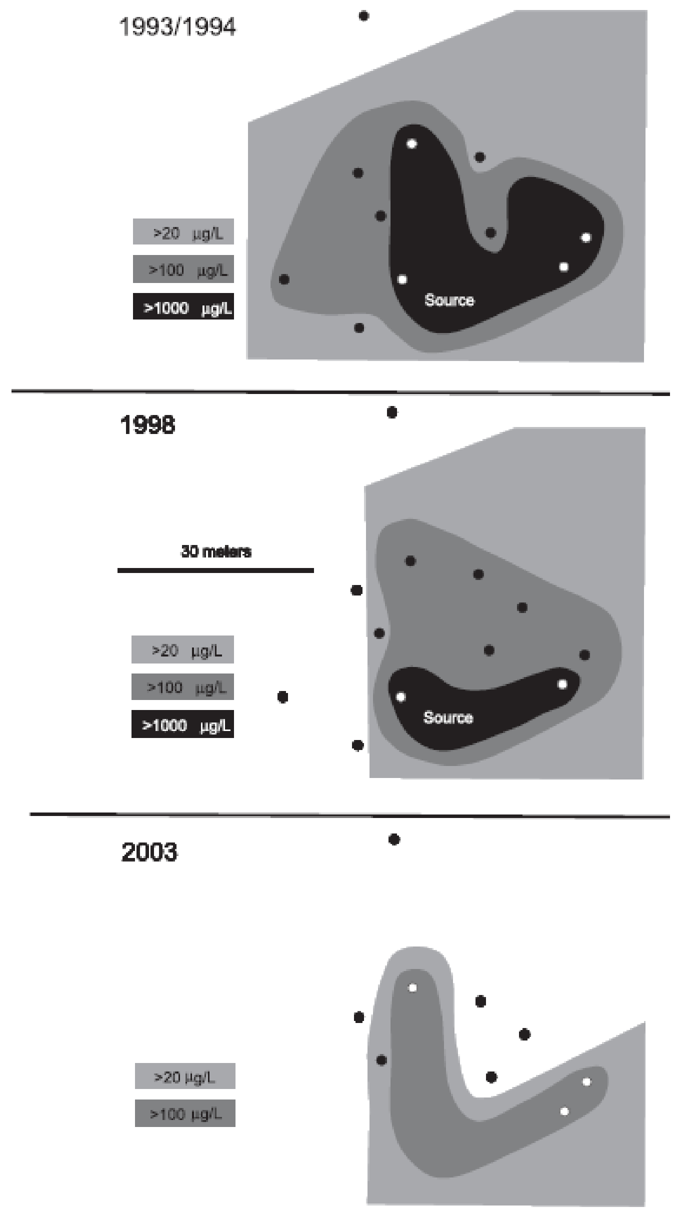






Parsippany, NJ

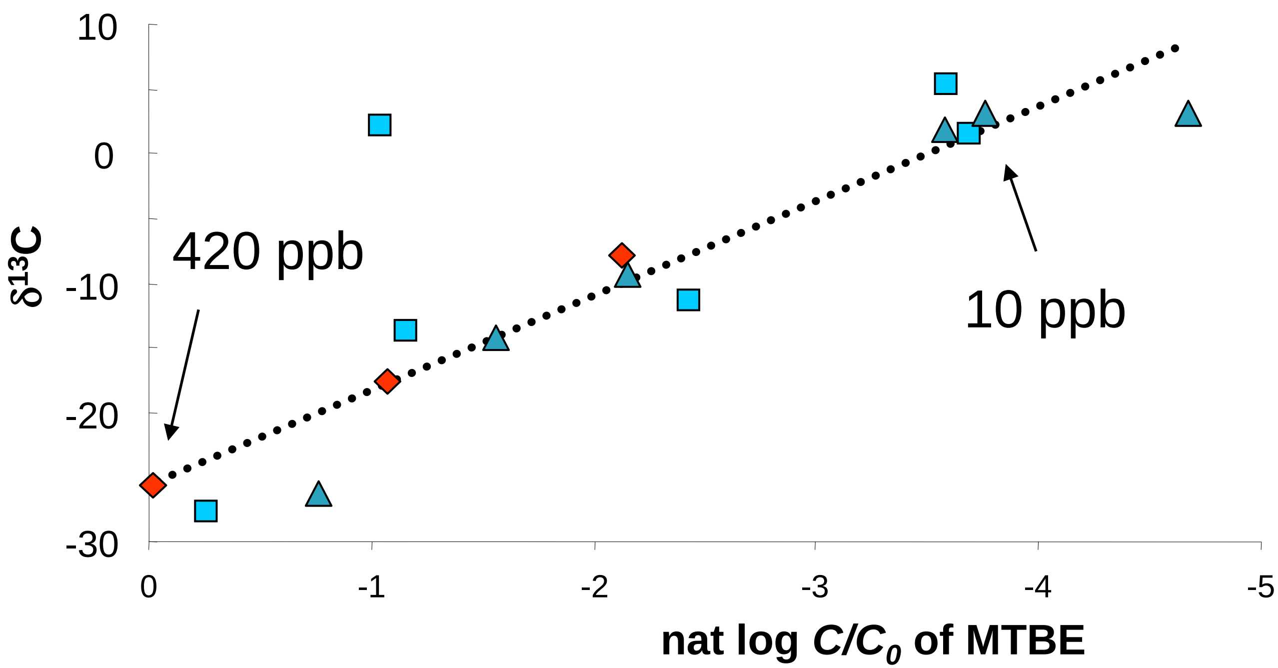
- Historical trend of shrinking MtBE plume
- CSIA performed in 2000-2002



after Wilson et al., 2005

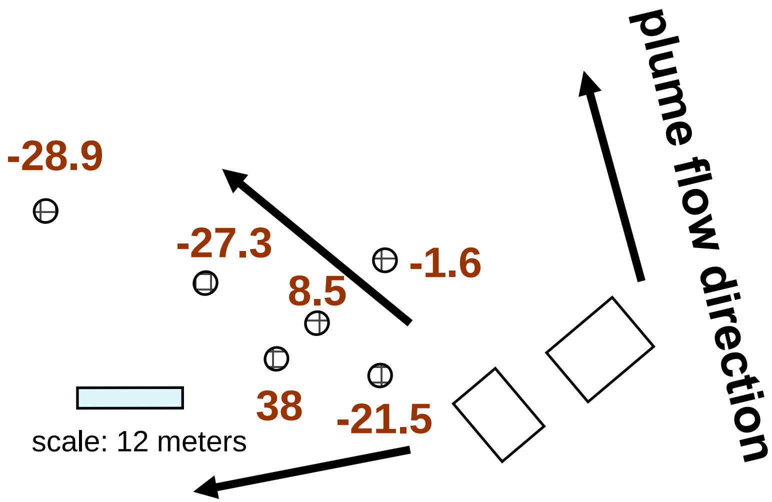
Parsippany, NJ

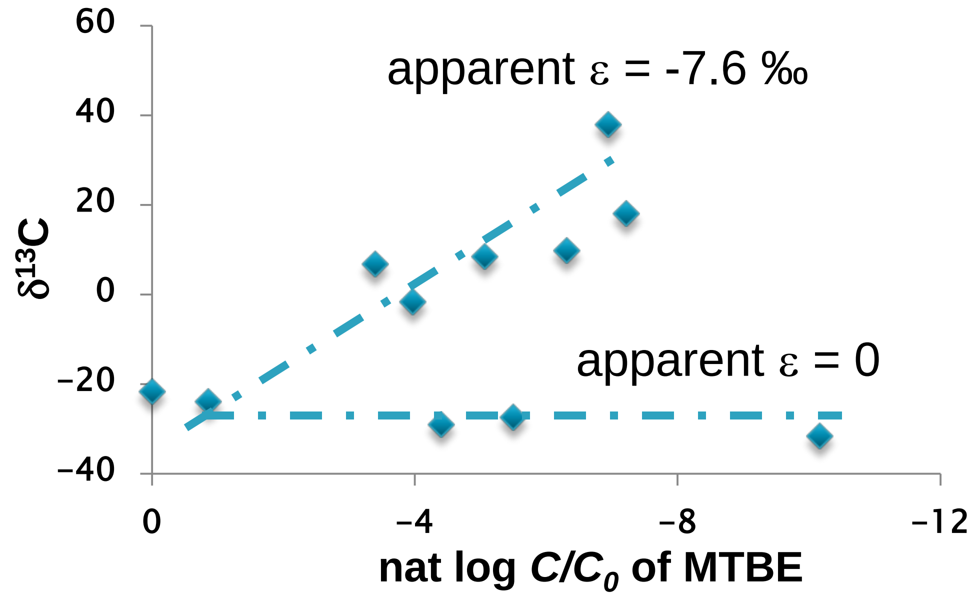
Very good match to the Rayleigh model. apparent enrichment factor (ε) approx. −8 ‰.



Dana Point, CA

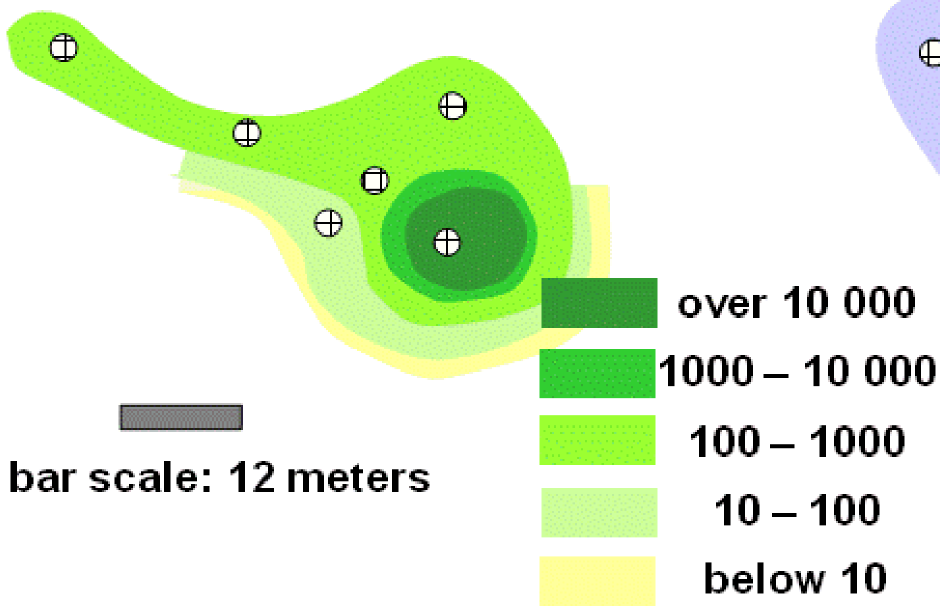
MTBE $\delta^{13}C$ values



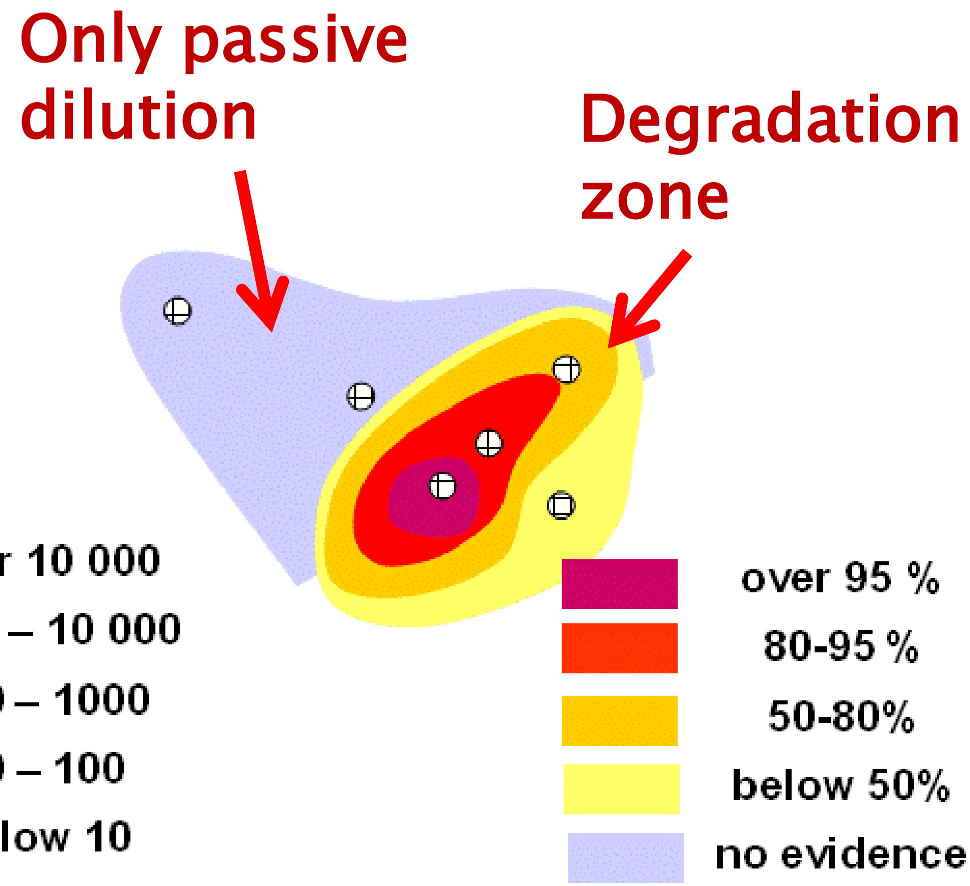


- Some data points follow a trend similar to that at Parsippany, NJ
- Some data points do not conform do Rayleigh model (show no fractionation)

Dana Point, CA



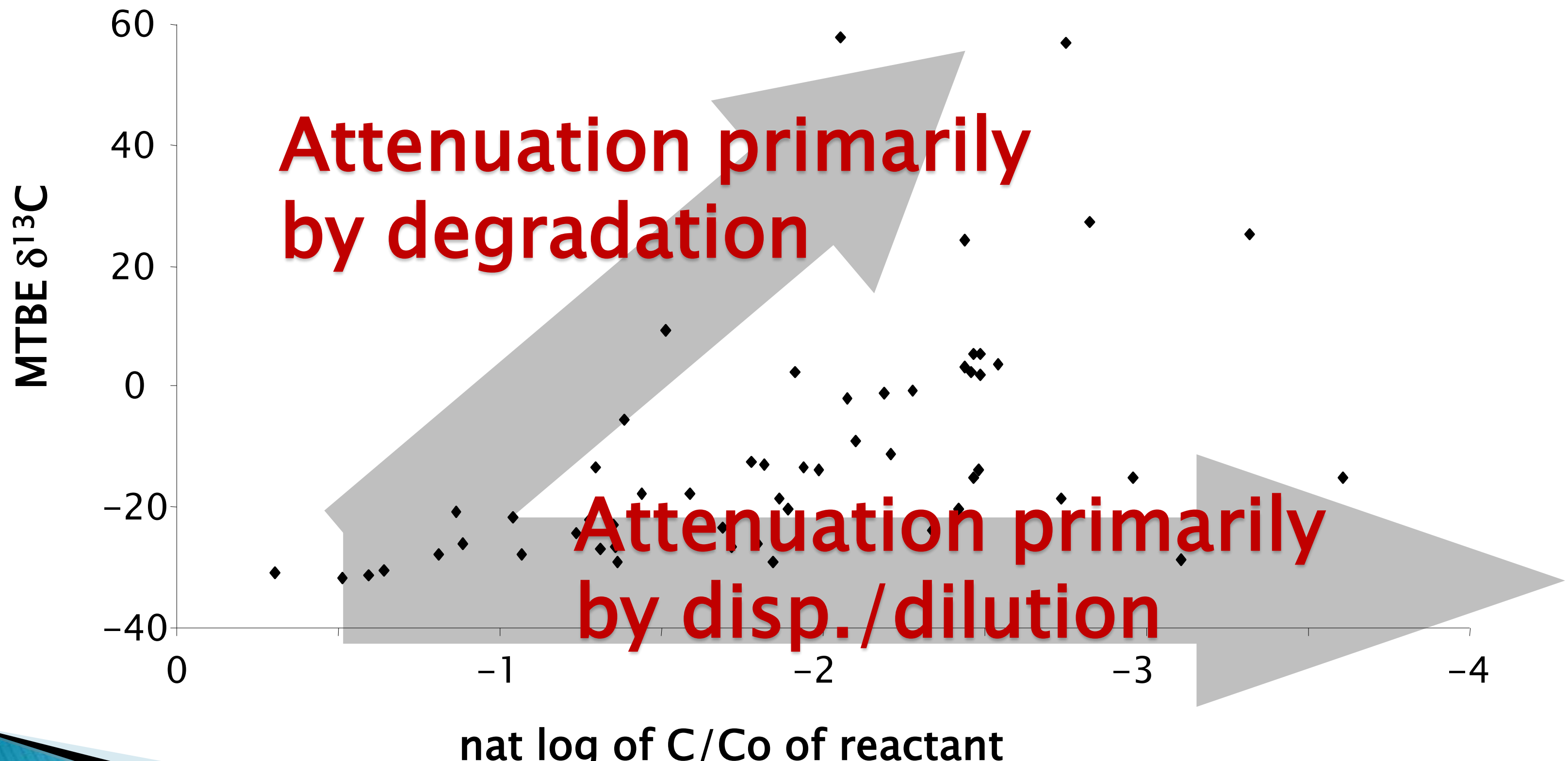
MtBE ug/L



Mass removal calculated by Rayleigh Eq.

Isotope Ratios in Degradation vs Dilution Scenarios

Example: Pooled data from MtBE sites in CA



Summary

- CSIA permits determination of C, Cl and H isotope ratios in individual chlorinated VOCs
- CSIA data are informative in contaminant source fingerprinting and in in-situ remediation assessment
- Evidence of mass destruction provided by characteristic changes of isotope ratios (isotope fractionation)
- Data interpretation utilizes the so-called Rayleigh model (see the following presentation by Dr. Wilson).

Questions?

Contact:

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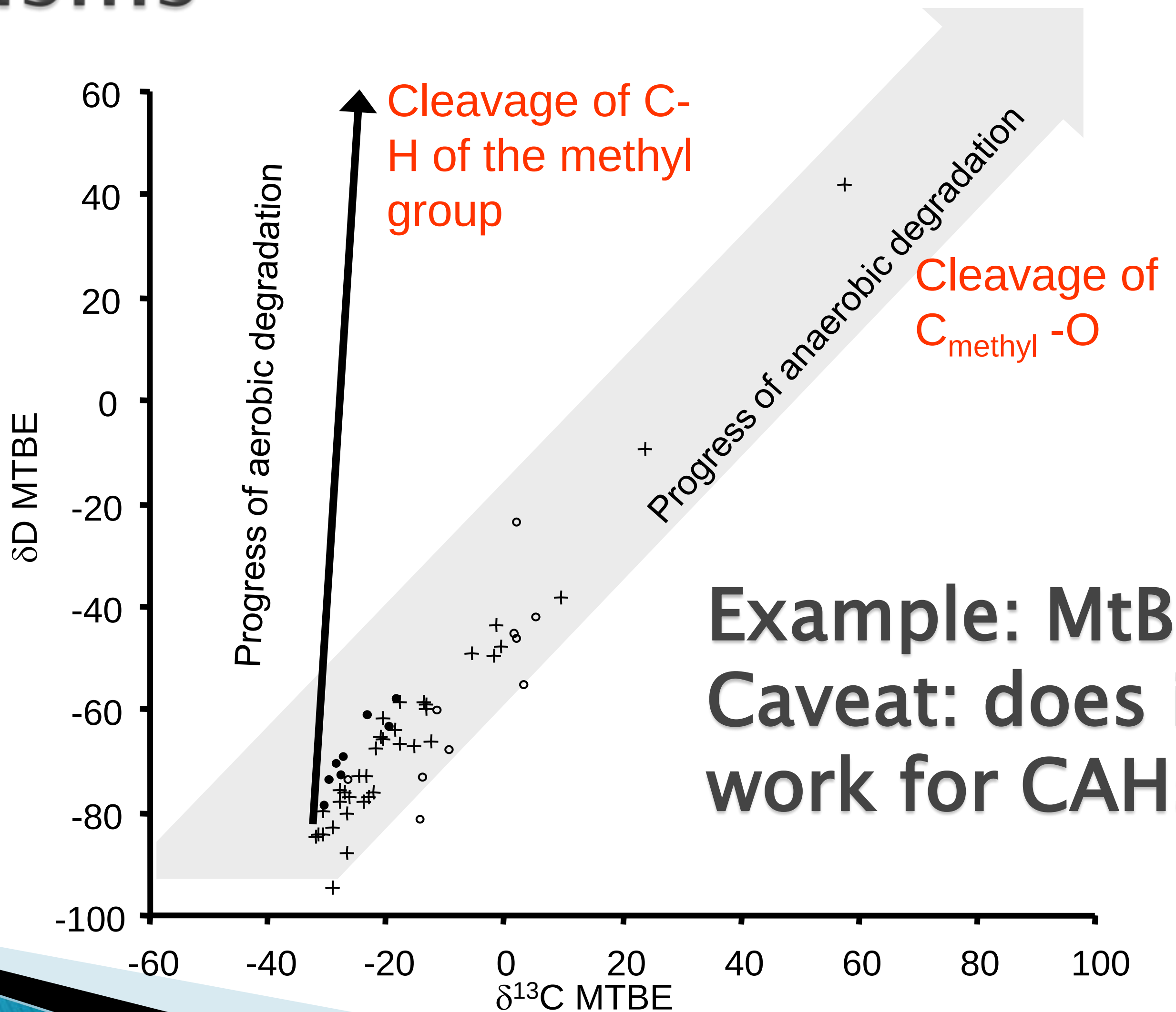
2D-CSIA: Identification of Reaction Mechanisms



Example: MtBE. Caveat: does it work for CAHs?